

Claims

1.-27. (Cancelled)

28. (Currently amended) A process for depositing a zinc alloy protective coating on aluminum or aluminum based alloy substrates which comprises

(A) immersion plating an aluminum or aluminum based alloy substrate by immersing the substrate in an aqueous acidic immersion plating solution having a pH of from about 3.5 to about 6.5 and comprising zinc ions, nickel and/or cobalt ions, fluoride ions and at least one inhibitor provided the solution is free of cyanide ions for a period of time sufficient to deposit the desired coating, and

(B) removing the coated substrate from the immersion plating solution, wherein the at least one inhibitor is (i) selected from nitrogen-containing disulfides; alkali metal thiocyanates; thiocarbamates; nitrogen-containing heterocyclic compounds; mercapto substituted nitrogen-containing heterocyclic compounds; thioacids; thioalcohols; compounds characterized by the formula



wherein each R is independently hydrogen or an alkyl, alkenyl, or aryl group, and Y is XR^1 , NR_2 or $N(H)NR_2$; wherein X is O or S and R^1 is hydrogen or an alkali metal; and mixtures thereof; or

~~——(ii)——at least one nitrogen-containing heterocyclic compound or mercapto substituted nitrogen-containing heterocyclic compound, or mixtures thereof.~~

29. (Original) The process of claim 28 wherein the surface of the aluminum or aluminum based alloy is cleaned, etched and desmutted prior to immersion in the immersion plating solution.

30. (Original) The process of claim 29 wherein the cleaning is performed with an alkaline, acidic, or solvent cleaner, and the etching is performed with an alkaline or acid etching solution.

31. (Original) The process of claim 29 wherein the aluminum or aluminum based alloy is rinsed with water after each of the cleaning, etching, desmutting, and immersion plating steps.

32.-35. (Cancelled)

36. (Currently amended) A process for depositing a zinc alloy protective coating on aluminum or aluminum based alloy substrate which comprises

(A) immersion plating the substrate by immersing the substrate in an aqueous acidic immersion plating solution having a pH of from about 4 to about 6 and comprising:

from about 10 to about 30 g/l of zinc ions,
 from about 20 to about 50 g/l of nickel and/or cobalt ions,
 from about 0.5 to about 10 g/l of fluoride ions, and
 from about 0.005 to about 0.05 g/l of an inhibitor for a period of time

sufficient to deposit the desired coating, and

(B) removing the coated substrate from the immersion plating solution, wherein the at least one inhibitor is (†) selected from nitrogen-containing disulfides; alkali metal thiocyanates; thiocarbamates; nitrogen-containing heterocyclic compounds; mercapto substituted nitrogen-containing heterocyclic compounds; thioacids; thioalcohols; compounds characterized by the formula



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wherein each R is independently hydrogen or an alkyl, alkenyl, or aryl group, and Y is XR^1 , NR_2 or $N(H)NR_2$; wherein X is O or S and R^1 is hydrogen or an alkali metal; and mixtures thereof; or

~~(ii) at least one nitrogen-containing heterocyclic compound or mercapto substituted nitrogen-containing heterocyclic compound, or mixtures thereof.~~

37. (Original) The process of claim 36 wherein the surface of the substrate is cleaned, etched and desmuted prior to immersion in the immersion plating solution.

38. (Original) The process of claim 37 wherein the cleaning is performed with an alkaline, acidic, or solvent cleaner, and the etching is performed with alkaline or acid etching solution.

39. (Previously presented) The process of claim 37 wherein the substrate is rinsed with water after each of the cleaning, etching, desmutting, and immersion plating steps.

40. (Currently amended) A process for depositing a metal coating on an aluminum or aluminum alloy substrate comprising

(A) applying an immersion zinc alloy protective coating on the substrate by immersion plating the substrate in an aqueous acidic immersion plating solution having a pH of from about 3.5 to about 6.5 and comprising zinc ions, nickel and/or cobalt ions, fluoride ions and at least one inhibitor provided the solution is free of cyanide ions for a period of time sufficient to deposit the desired coating, and

(B) plating the zinc alloy coated substrate using an electroless or electrolytic metal plating solution,

wherein the at least one inhibitor is (i) selected from nitrogen-containing disulfides; alkali metal thiocyanates; thiocarbamates; nitrogen-containing heterocyclic compounds; mercapto substituted nitrogen-containing heterocyclic compounds; thioacids; thioalcohols; compounds characterized by the formula



wherein each R is independently hydrogen or an alkyl, alkenyl, or aryl group, and Y is XR^1 , NR_2 or $N(H)NR_2$; wherein X is O or S and R^1 is hydrogen or an alkali metal; and mixtures thereof; or

~~(ii) at least one nitrogen-containing heterocyclic compound or mercapto substituted nitrogen-containing heterocyclic compound, or mixtures thereof.~~

41. (Original) The process of claim 40 wherein the surface of the substrate is subjected to cleaning, acid etching and desmutting, prior to immersion in the immersion plating solution.

42. (Original) The process of claim 41 wherein the cleaning is performed with an alkaline, acidic, or solvent cleaner, and the etching is performed with alkaline or acid etching solution.

43-49. (Cancelled)

50. (Previously presented) The process of claim 28 wherein the plating solution also contains one or more metal complexing agents.

51. (Previously presented) The process of claim 28 wherein the plating solution also contains one or more additional metal ions selected from copper ions, iron ions, manganese ions, magnesium ions and zirconium ions.

52-54. (Cancelled)

55. (Currently amended) The process of claim 28 wherein the heterocyclic compound is selected from pyrroles, imidazoles, benzimidazoles, pyrazoles, triazoles, benzotriazoles, tetrazoles, pyridines, dipyridyls, piperazines, pyrazines, piperidines, pyrimidines, thiazoles, thiazolines, thiazolidines, rhodamines, and morpholines.

56. (Previously presented) The process of claim 28 wherein the inhibitor is the mercapto substituted nitrogen containing heterocyclic compound.

57. (Previously presented) The process of claim 28 wherein the plating solution contains
from about 1 to about 150 g/l of zinc ions, and
from about 5 to about 250 g/l of nickel and/or cobalt ions.

58. (Previously presented) The process of claim 28 wherein the plating solution contains from about 0.0005 to about 5 g/l of the inhibitor.

59. (Previously presented) The process of claim 28 wherein the plating solution is free of aliphatic amines and aliphatic hydroxylamines.

60. (Currently amended) A process for depositing a zinc alloy protective coating on aluminum or aluminum based alloy substrate which comprises

(A) immersion plating the substrate by immersing the substrate in an aqueous acidic immersion plating solution having a pH of from about 3.5 to about 6.5 and comprising:

from about 1 to about 150 g/l of zinc ions,

from about 5 to about 250 g/l of nickel and/or cobalt ions,

from about 0.005 to about 100 g/l of fluoride ions provided the solution is free of cyanide ions, and

from about 0.005 to about 100 g/l of an inhibitor for a period of time sufficient to deposit the desired coating, and

(B) removing the coated substrate from the immersion plating solution, wherein the at least one inhibitor is (i) selected from nitrogen-containing disulfides; alkali metal thiocyanates; thiocarbamates; nitrogen-containing heterocyclic compounds; mercapto substituted nitrogen-containing heterocyclic compounds; thioacids; thioalcohols; compounds characterized by the formula



wherein each R is independently hydrogen or an alkyl, alkenyl, or aryl group, and Y is XR^1 , NR_2 or $N(H)NR_2$; wherein X is O or S and R^1 is hydrogen or an alkali metal; and mixtures thereof; or

~~—— (ii) — at least one nitrogen-containing heterocyclic compound or mercapto substituted nitrogen-containing heterocyclic compound, or mixtures thereof.~~

61. (Previously presented) The process of claim 60 wherein the plating solution also contains at least one metal complexing agent.

62. (Previously presented) The process of claim 61 wherein the metal complexing agent is selected from an acetate, citrate, glycollate, lactate, maleate, pyrophosphate, tartrate, gluconate, or glucoheptonate, and mixtures thereof.

63-65. (Cancelled)

66. (Currently amended) The process of claim 60 wherein the heterocyclic compound is selected from pyrroles, imidazoles, benzimidazoles, pyrazoles, triazoles, benzotriazoles, dipyridyls, tetrazoles, thiazoles, thiazolines, thiazolidines, pyridines, piperazines, pyrazines, piperidines, pyrimidines, and morpholines.

67. (Previously presented) The process of claim 60 wherein the inhibitor is the mercapto substituted nitrogen containing heterocyclic compound.

68. (Previously presented) The process of claim 60 wherein the plating solution has a pH of from about 4 to about 6.

69. (Previously presented) The process of claim 60 wherein the plating solution also contains one or more metal ions selected from copper ions, iron ions, manganese ions, magnesium ions and zirconium ions.

70. (Previously presented) The process of claim 60 wherein the plating solution is free of aliphatic amines and aliphatic hydroxylamines.

71. (Previously presented) The process of claim 36 wherein the plating solution also contains from about 1 to about 250 g/l of at least one metal complexing agent.

72. (Previously presented) The process of claim 36 wherein the inhibitor is the mercapto substituted nitrogen containing heterocyclic compound.

73. (Currently amended) The process of claim 36 wherein the heterocyclic compound is selected from pyrroles, imidazoles, benzimidazoles, pyrazoles, triazoles, benzotriazoles, pyridines, dipyridyls, piperazines, pyrazines, piperidines, pyrimidines, tetrazoles, thiazoles, thiazolines, thiazolidines, rhodamines, and morpholines.

74. (Previously presented) The process of claim 36 wherein the plating solution is free of aliphatic amines and aliphatic hydroxylamines.

75. (Previously presented) The process of claim 71 wherein the metal complexing agent is selected from an acetate, citrate, glycollate, lactate, maleate, pyrophosphate, tartrate, gluconate, or glucoheptonate, and mixtures thereof.

76. (Previously presented) The process of claim 36 wherein the plating solution further comprises one or more metal ions selected from copper ions, iron ions, manganese ions, magnesium ions and zirconium ions.

77. (Previously presented) The process of claim 41 wherein the aluminum or aluminum based alloy is rinsed with water after each of the cleaning, etching, desmutting, and immersion plating steps.

78. (Previously presented) The process of claim 40 wherein the plating solution contains
from about 1 to about 150 g/l of zinc ions, and
from about 5 to about 250 g/l of nickel and/or cobalt ions.

79. (Previously presented) The process of claim 40 wherein the plating solution contains from about 0.0005 to about 5 g/l of the inhibitor.

80. (Previously presented) The process of claim 40 wherein the plating solution also contains from about 1 to about 250 g/l of at least one metal complexing agent.

81. (Previously presented) The process of claim 80 wherein the metal complexing agent is selected from an acetate, citrate, glycollate, lactate, maleate, pyrophosphate, tartrate, gluconate, or glucoheptonate, and mixtures thereof.

82. (Currently amended) The process of claim 40 wherein the heterocyclic compound is selected from pyrroles, imidazoles, benzimidazoles, pyrazoles, triazoles, benzotriazoles, pyridines, dipyridyls, piperazines, pyrazines, piperidines, pyrimidines, tetrazoles, thiazoles, thiazolines, thiazolidines, rhodamines, and morpholines.

83. (Previously presented) The process of claim 40 wherein the inhibitor is the mercapto substituted nitrogen containing heterocyclic compound.

84. (Previously presented) The process of claim 40 wherein the plating solution is free of aliphatic amines and aliphatic hydroxylamines.

85. (Previously presented) The process of claim 40 wherein the plating solution further comprises one or more metal ions selected from copper ions, iron ions, manganese ions, magnesium ions and zirconium ions.

86. (Previously presented) The process of claim 40 wherein the plating solution has a pH of from about 4 to about 6.

87. (Previously presented) The process of claim 40 wherein the solution further comprises from about 0.5 to about 10 g/l of fluoride ions.

88. (Previously presented) The process of claim 60 wherein the surface of the aluminum or aluminum based alloy is cleaned, etched and desmutted prior to immersion in the immersion plating solution.

89. (Previously presented) The process of claim 88 wherein the cleaning is performed with an alkaline, acidic, or solvent cleaner, and the etching is performed with an alkaline or acid etching solution.

90. (Previously presented) The process of claim 88 wherein the aluminum or aluminum based alloy is rinsed with water after each of the cleaning, etching, desmutting, and immersion plating steps.

91. (Previously presented) The process of claim 28 wherein the solution further comprises from about 0.5 to about 10 g/l of fluoride ions.

92. (Previously presented) The process of claim 28 wherein the plating solution has a pH of from about 4 to about 6.

93. (Previously presented) The process of claim 50 wherein the metal complexing agent is selected from an acetate, citrate, glycollate, lactate, maleate, pyrophosphate, tartrate, gluconate, or glucoheptonate, and mixtures thereof.